Published in "Angewandte Chemie International Edition 49(4): 708 - 711, 2010"
which should be cited to refer to this work.

Multiresponsive Reversible Gels Based on Charge-Driven Assembly**

Marc Lemmers, Joris Sprakel, Ilja K. Voets, Jasper van der Gucht, and Martien A. Cohen Stuart*

Multiresponsive materials are interesting for a wide range of applications, as their properties can be tuned with external triggers. A promising class of responsive materials is that of physically cross-linked polymer networks. These transient networks are typically assembled from telechelic polymers[1–5] or linear triblock copolymers,[6–9] although other architectures have been investigated as well.[10–14] Most widely studied are ABA triblock copolymers with hydrophobic end groups and a hydrophilic middle block. These so-called "associative thickeners" have the ability to change the rheological properties of solvents at relatively low concentrations. For this reason, they are widely used as rheology modifiers in industry. However, the hydrophobic interaction on which the gelation of these "classical" associative thickeners is based can be tuned only by changing the temperature or solvent, or by synthesizing a new molecule. To have more control over the gel properties, reversibly formed gels based on an entirely different driving force are needed.

Herein we present a novel class of multiresponsive reversible gels based on the coassembly of a triblock copolymer having two charged end blocks with an oppositely charged homopolymer. These reversible gels respond not only to changes in temperature and concentration but also to ionic strength, cationic/anionic composition and, if weak polyelectrolytes are used, pH value.

Mixing two aqueous solutions of oppositely charged polyelectrolytes generally leads to phase separation.[15–17] Addition of a neutral solvophilic block to the polyelectrolyte chain can prevent macroscopic phase separation. Instead, a microscopic phase separation occurs, leading to micelles consisting of a core containing a polyelectrolyte complex stabilized by a corona of neutral solvophilic blocks.[18–22]

When triblock copolymers with two charged end blocks are used instead of diblock copolymers, flowerlike micelles can be formed (Figure 1 a). These micelles are stabilized by a corona of looped solvophilic chains. At polymer concentrations above a critical gel concentration (C_{gel}), the triblock copolymer will bridge between two different micellar cores. The micelles thus become connected with each other, leading to the formation of a reversible gel (Figure 1 b).

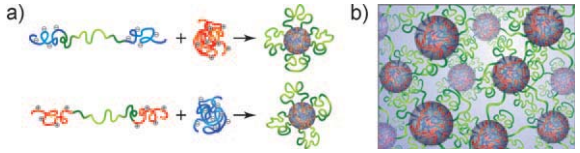
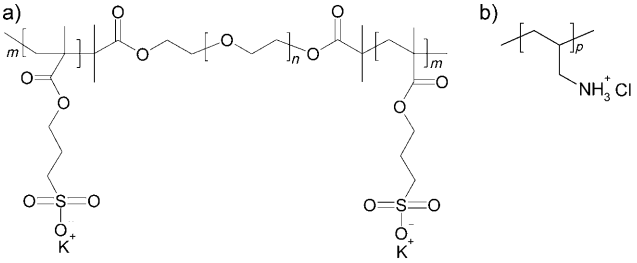


Figure 1. Schematic representation of the formation of reversible gels based on charge-driven assembly. a) Monomers associate into flower-like micelles in dilute solution. b) The neutral middle block forms bridges between the micellar cores to form a transient network.

ABA triblock copolymers with negatively charged end blocks and a water-soluble neutral middle block ($PSPMA_{28}$–PEO_{230}–$PSPMA_{28}$) were synthesized by atom transfer radical polymerization (see the Supporting Information).[23–26] The molecular structure is given in Scheme 1 a. Poly(allylamine hydrochloride)$_{160}$ (PAH_{160}) was used as oppositely charged homopolymer (Scheme 1 b).



Scheme 1. Molecular structures of a) the negatively charged triblock copolymer $PSPMA_{28}$-PEO_{230}-$PSPMA_{28}$ ($n \approx 230$; $m \approx 28$) and b) the positively charged homopolymer PAH_{160} ($p \approx 160$).

To investigate the coassembly of $PSPMA_{28}$–PEO_{230}–$PSPMA_{28}$ with PAH_{160} in dilute solution, dynamic light scattering (DLS) titrations were used. We define a charge composition variable f^+ [Eq. (1)]:[22]

$$f^+ = \frac{[+]}{[+]+[-]} \quad (1)$$

which is the concentration of positively chargeable groups [+] divided by the total amount of chargeable groups [−] + [+]. Upon titrating either of the two components to the other, complexes are formed, as indicated by an increase in scattered light intensity. The scattered light intensity increases up to the point of charge stoichiometry, after which it decreases again (Figure 2). The complexes that are formed in these dilute solutions are flowerlike micelles with a hydrodynamic radius of approximately 20 nm.

When $PSPMA_{28}$–PEO_{230}–$PSPMA_{28}$ and PAH_{160} are mixed at higher concentrations, a highly viscous and transparent gel is formed spontaneously (movie available as Supporting Information). This result indicates that an interconnected micellar network is indeed formed.

[*] M. Lemmers, Dr. J. van der Gucht, Prof. Dr. M. A. Cohen Stuart
Laboratory of Physical Chemistry and Colloid Science
Wageningen University
Dreijenplein 6, 6703 HB, Wageningen (The Netherlands)
Fax: (+31) 317-483-777
E-mail: marc.lemmers@wur.nl
Dr. J. Sprakel
School of Engineering and Applied Sciences, Department of Physics
Harvard University, Cambridge, MA 02138 (USA)
Dr. I. K. Voets
Institut Adolphe Merkle, Université de Fribourg (Switzerland)
M. Lemmers, Dr. J. Sprakel
Dutch Polymer Institute, Eindhoven (The Netherlands)

[**] We acknowledge Dr. A. T. M. Marcelis for his help in the synthesis of the triblock copolymer, Prof. Armes for providing a detailed protocol for the triblock copolymer synthesis, and Prof. Detrembleur for doing the SEC analysis. This research is funded by the Dutch Polymer Institute (DPI), project no 657. I.K.V. is supported by a European Marie Curie Fellowship (FP7-PEOPLE-IEF-2008, Contract No. 236723) and by the Adolphe Merkle Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905515.

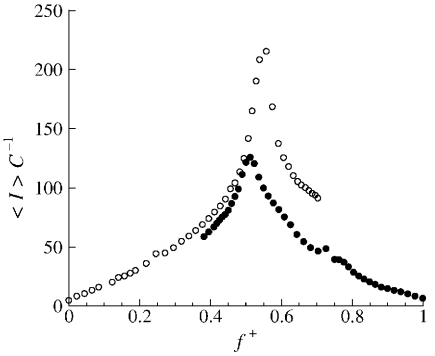


Figure 2. The average scattered light intensity, normalized by the total polymer concentration, as a function of the composition variable f^+. The titration is performed at low polymer concentration (ca. 1 g L^{-1}) and at [KCl] = 0.2 M. The driving force for complex coacervation is strongest at charge stoichiometry, $f^+ = 0.5$. ○ shows titration of a solution of PAH_{160} to a solution of $PSPMA_{28}$–PEO_{230}–$PSPMA_{28}$; ● shows the reverse experiment. The difference in scattering between the two measurements is due to non-equilibrium structures.

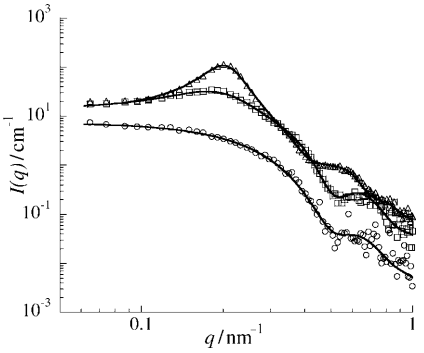


Figure 3. X-ray scattering curves for three different polymer concentrations at fixed salt concentration of 0.4 M KCl; ○ 1%, □ 8%, and △ 16%(w/w).

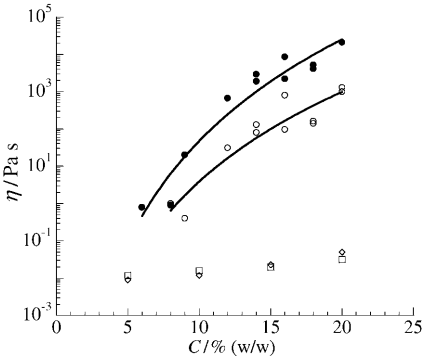


Figure 4. Viscosity as a function of the total polymer concentration at a fixed salt concentration of 0.4 M KCl. The viscosity of the reversible gel is given for two different temperatures. ● 5 °C data points, ○ 30 °C data points. The lines are drawn to guide the eye. The viscosities of solutions of PEG_{230} and PAH_{160} in water at 5 °C and 0.4 M KCl are depicted by ◇ and □, respectively.

To further investigate the shape of, and interactions between, the micelles, small-angle X-ray scattering (SAXS) measurements were performed. Excellent agreement between experimental SAXS data and fits can be achieved by using a form factor for polydisperse (Gaussian) homogeneous spheres, in combination with an effective structure factor for the higher concentrations (Figure 3). Generalized indirect Fourier transform[27–29] analysis indicates that the scattering objects, the micellar cores, have a spherical shape with a radius of gyration $R_g = (8.1 \pm 0.4)$ nm. For samples with more than 4% (w/w) polymer, the structure factor becomes more pronounced, exhibiting a peak for the gel samples at $q \approx 0.21$ nm^{-1}. This value corresponds to an intermicellar distance of approximately 30 nm.

The viscosity (η) of the reversible gels as a function of concentration (C) was investigated with rheometry. A surprisingly strong dependence is found: η increases by more than six orders of magnitude over a fourfold increase in concentration (Figure 4). The C_{gel} is approximated to be 4% (w/w) by extrapolating the data points to the viscosity of a 5 °C PEG_{230} solution. The gels are responsive to temperature, because the viscosity decreases roughly by an order of magnitude upon an increase in temperature by 25 °C.

Charge-driven assemblies are responsive to ionic strength. The scattered light intensity decreases with increasing [KCl], thus indicating that the driving force for micelle formation is weakened with increasing salt concentration (Figure 5a). From this figure, a critical KCl concentration $I_{cr} = 1.7$ M KCl can be determined. The light scattering data are in agreement with the rheological data. The viscosity decreases strongly as a function of salt concentration (Figure 5b). As I_{cr} is approached, η approaches the value of a 16% (w/w) PEG_{230} solution, because of complete disintegration of the micelles. Hence, an almost solid-like gel can be transformed into a water-like fluid simply by adding salt (movie available as Supporting Information).

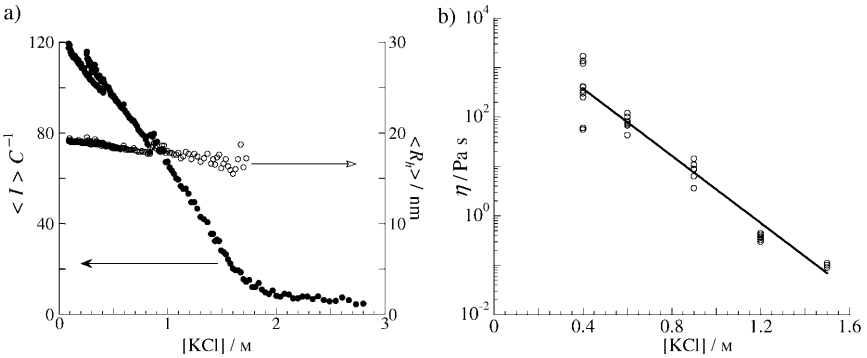


Figure 5. Influence of ionic strength in dilute solutions (a) and concentrated solutions (b). a) Effect of ionic strength on the formation of flowerlike micelles. The average scattered light intensity normalized by the total polymer weight concentration ($\langle I \rangle C^{-1}$, ●, left axis) and average hydrodynamic radius ($\langle R_h \rangle$, ○, right axis) as a function of [KCl]. b) Viscosity of a 16% (w/w) gel at 20 °C as a function of [KCl]. Data points are given by ○; the line is an exponential fit through the data points.

Since the homopolymer used in this particular system is a weak polyelectrolyte, the system also responds to pH value. Upon increasing the pH value of a dilute solution of micelles, the number of micelles in solution slowly decreases, as indicated by a decrease in scattered light intensity (Figure 6a). This effect is due to discharging of the homopolymer PAH_{160} at $pH \geq 8$. The decrease in the number of micelles at $pH \geq 8$ is also noticeable in the gels. Addition of KOH to an 18% (w/w) gel at 0.4 M KCl and $f^+ = 0.5$ drastically decreases the viscosity of the gel (Figure 6b,c).

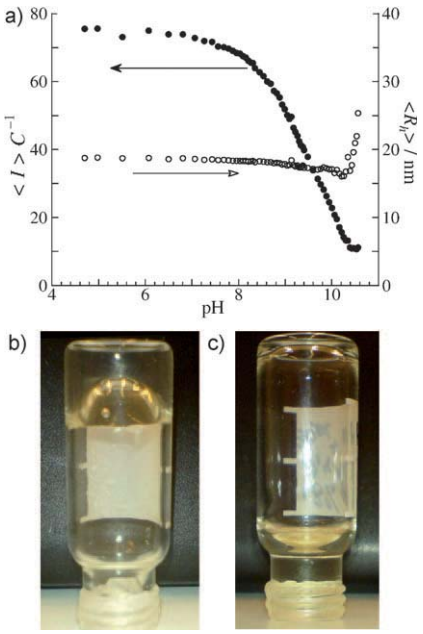


Figure 6. Influence of pH value on the coassembly of $PSPMA_{28}$-PEO_{230}-$PSPMA_{28}$ and PAH_{160} at 0.4 M KCl. a) Average scattered light intensity normalized by total polymer weight concentration (●, left axis) and average hydrodynamic radius (○, right axis) as a function of pH value. b) The viscosity of a 18% (w/w) gel is high enough to take a picture with the gel sticking at the bottom of the vial. c) Same gel as in (b), but with KOH added, leading to $pH \approx 9$. The viscosity has decreased such that the gel flows directly to the bottom when the vial is turned upside down.

In conclusion, we have presented a new class of multiresponsive, reversible gels based on charge-driven coassembly of two water-soluble components: an ABA triblock copolymer with a hydrophilic middle block and polyelectrolyte end blocks and an oppositely charged homopolymer. Based on SAXS data we conclude that these reversible gels consist of a network of interconnected polyelectrolyte complex micelles. The properties of this network can be tuned by varying the concentration, temperature, ionic strength, pH value, and charge composition.

In general, the multiresponsiveness of this new class of gels, combined with the ability to choose both the type and length of each of the individual components, allows for an almost endless variety of properties. This variability makes charge-driven reversible gels interesting candidates for a multitude of possible applications.

[1] R. A. Register, M. Foucart, R. Jerome, Y. S. Ding, S. L. Cooper, *Macromolecules* **1988**, *21*, 1009–1015.
[2] R. D. Jenkins, C. A. Silebi, M. S. El-Asser, *ACS Symp. Ser.* **1991**, *462*, 222–233.
[3] T. Annable, R. Buscall, R. Ettelaie, D. Whittlestone, *J. Rheol.* **1993**, *37*, 695–726.
[4] P. Kujawa, H. Watanabe, F. Tanaka, F. M. Winnik, *Eur. Phys. J. E* **2005**, 129–137.
[5] J. Sprakel, E. Spruijt, M. A. C. Stuart, N. A. M. Besseling, M. P. Lettinga, J. van der Gucht, *Soft Matter* **2008**, *4*, 1696–1705.
[6] C. Tsitsilianis, I. Iliopoulos, G. Ducouret, *Macromolecules* **2000**, *33*, 2936–2943.
[7] F. Bossard, T. Aubry, G. Gotzamanis, C. Tsitsilianis, *Soft Matter* **2006**, *2*, 510–516.
[8] N. Stavrouli, T. Aubry, C. Tsitsilianis, *Polymer* **2008**, *49*, 1249–1256.
[9] P. J. Skrzeszewska, F. A. de Wolf, M. W. T. Werten, A. Moers, M. A. C. Stuart, J. van der Gucht, *Soft Matter* **2009**, *5*, 2057–2062.
[10] V. Tirtaatmadja, K. C. Tam, R. D. Jenkins, *Macromolecules* **1997**, *30*, 3271–3282.
[11] L. E. Bromberg, D. P. Barr, *Macromolecules* **1999**, *32*, 3649–3657.
[12] E. J. Regalado, J. Selb, F. Candau, *Macromolecules* **1999**, *32*, 8580–8588.
[13] A. C. Lara-Ceniceros, C. Rivera-Vallejo, E. J. Jimenez-Regalado, *Polym. Bull.* **2007**, *58*, 425–433.
[14] C. Tsitsilianis, N. Stavrouli, V. Bocharova, S. Angelopoulos, A. Kiriy, I. Katsampas, M. Stamm, *Polymer* **2008**, *49*, 2996–3006.
[15] F. Tiebackx, *Z. Chem. Ind. Kolloide* **1911**, *8*, 198–201.
[16] H. Bungenberg de Jong, H. Kruyt, *Proc. K. Ned. Akad. Wet.* **1929**, *32*, 849–856.
[17] H. Bungenberg de Jong, *Crystallisation Coacervation Flocculation*, Elsevier, Amsterdam, **1949**.
[18] A. Harada, K. Kataoka, *Macromolecules* **1995**, *28*, 5294–5299.
[19] A. Harada, K. Kataoka, *Science* **1999**, *283*, 65–67.
[20] A. V. Kabanov, T. K. Bronich, V. A. Kabanov, K. Yu, A. Eisenberg, *Macromolecules* **1996**, *29*, 6797–6802.
[21] M. A. Cohen Stuart, N. A. M. Besseling, R. G. Fokkink, *Langmuir* **1998**, *14*, 6846–6849.
[22] S. van der Burgh, A. de Keizer, M. A. Cohen Stuart, *Langmuir* **2004**, *20*, 1073–1084.
[23] K. Jankova, X. Y. Chen, J. Kops, W. Batsberg, *Macromolecules* **1998**, *31*, 538–541.
[24] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721–1723.
[25] J. S. Wang, K. Matyjaszewski, *Macromolecules* **1995**, *28*, 7901–7910.
[26] G. Masci, D. Bontempo, N. Tiso, M. Diociaiuti, L. Mannina, D. Capitani, V. Crescenzi, *Macromolecules* **2004**, *37*, 4464–4473.
[27] O. Glatter, *J. Appl. Crystallogr.* **1977**, *10*, 415–421.
[28] B. Weyerich, J. Brunner-Popela, O. Glatter, *J. Appl. Crystallogr.* **1999**, *32*, 197–209.
[29] A. Bergmann, G. Fritz, O. Glatter, *J. Appl. Crystallogr.* **2000**, *33*, 1212–1216.